

Polymers with Pendant Isocyanate Groups. III. Synthesis and Properties of Poly(styrene-co- Acrylonitrile-co-Styrylisocyanate)*

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Synopsis

The terpolymer poly(styrene-co-acrylonitrile-co-styrylisocyanate) was synthesized by radical initiation directly from styrene, acrylonitrile, and cinnamoyl azide. The monomer feed-terpolymer composition relationship was determined by Slocombe's triangular graph. The solubility, intrinsic viscosity, and melting range of the various terpolymers and the chemical reactions of the pendant isocyanate groups toward alcohol and amines were investigated.

INTRODUCTION

In two previous papers, the copolymerization of cinnamoyl azide with styrene¹ and with acrylonitrile² has been reported. In both cases the cinnamoyl azide rearranged during copolymerization to styrylisocyanate, and copolymers of styrene-styrylisocyanate and of acrylonitrile-styrylisocyanate were obtained. Whereas the former copolymer is very stable at atmospheric conditions, the second is very sensitive to moisture.

In the present paper we wish to report on the terpolymerization of styrene, acrylonitrile, and cinnamoyl azide and on some properties of the new terpolymers, which due to rearrangement of the azide, are composed of styrene, acrylonitrile, and styrylisocyanate.

EXPERIMENTAL

Materials and Preparation of Monomers. Acrylonitrile, styrene, and the initiator α,α' -azobisisobutyronitrile (AIBN) were purified in the usual manner, and the comonomer cinnamoyl azide was synthesized as described before.¹

Terpolymerization. The terpolymerizations were carried out at 60°C during 20 min with AIBN (0.1 mol %) as initiator, as described previously.¹ The total monomer feed in the reaction tubes was $M_1 + M_2 + M_2 \cong 0.1$ mol. The reaction products were precipitated by methanol; they were further purified by reprecipitation from their solution in MEK with methanol, followed by washing with petrol ether (bp: 40–60°C) and drying at 60°C and 0.1 mm Hg. The terpolymers were obtained as colorless powders, and their composition was determined by elemental analysis (C, H, N, and O content). The presence of the isocyanate and the nitrile groups was confirmed by ir spectroscopy.

Details on the conditions of the terpolymerizations and the results are summarized in Table I.

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TABLE I
 Terpolymerization of Styrene (M_1), Acrylonitrile (M_2), and Cinnamoylazide (M_3) to Low Conversion

Exp. No.	Monomer Feed (mol fraction)			Conversion (%)	C (%)	H (%)	N (%)	O (%)	Terpolymer			Melting Range (°C)	$[\eta]^a$ (dl/g)
	M_1	M_2	M_3						m_1	m_2	m_3		
74/1	0.677	0.107	0.215	~0.5	86.79	7.20	4.20	1.14	0.713	0.218	0.068	0.68	
74/2	0.574	0.213	0.212	~0.5	86.08	7.39	5.57	0.78	0.643	0.314	0.043		
74/3	0.677	0.215	0.107	~0.5	86.43	7.53	5.58	0.67	0.644	0.319	0.036	105-125	
74/4	0.60	0.30	0.10	~0.5	86.04	7.35	6.07	0.51	0.601	0.370	0.027	115-125	
74/5	0.80	0.10	0.10	~0.5	87.66	7.40	4.19	0.68	0.720	0.240	0.039	110-125	
74/6	0.60	0.20	0.20	~0.5	85.49	7.24	6.13	1.03	0.609	0.333	0.057	110-125	
74/7	0.50	0.40	0.10	~0.5	84.81	7.26	6.63	1.10	0.582	0.357	0.060		
74/8	0.50	0.30	0.20	~0.5	85.00	7.29	6.75	1.23	0.573	0.358	0.068	115-125	

^a Viscosity was determined with benzene solutions at 25°C.

Characterization. The ir spectra, intrinsic viscosity, solubility, and softening range of the terpolymers were determined as described before.¹

Chemical Reactions of the Terpolymer. The reactions of the terpolymer with ethanol and *n*-laurylamine were carried out in the same manner as described previously.¹

RESULTS AND DISCUSSION

The terpolymer styrene-acrylonitrile-styrylisocyanate was obtained by terpolymerization of styrene, acrylonitrile, and cinnamoyl azide. Similar to the copolymerization of the pairs styrene-cinnamoyl azide¹ and acrylonitrile-cinnamoyl azide,² in the present case also, the azide groups rearrange during the polymerization to isocyanate groups. Consequently, both the absorption bands of the nitrile group at 2240 cm^{-1} and of the isocyanate group at 2260 cm^{-1} are present in the ir spectra of all terpolymers (Fig. 1).

The relationship between the monomer feed and the molar composition of the obtained terpolymers, determined by polymerizations up to low conversion, is presented by Slocombe's triangle method (Fig. 2).³ It can be summarized as follows: generally the arrows point towards the azeotropic line, which connects the two binary azeotropic compositions of the pairs styrene-acrylonitrile (60/40)⁴ and styrene-cinnamoyl azide (93/7);¹ yet there is a stronger tendency towards the azeotropic region of the former pair.

The melting ranges of the various terpolymers are all of the same magnitude (Table I).

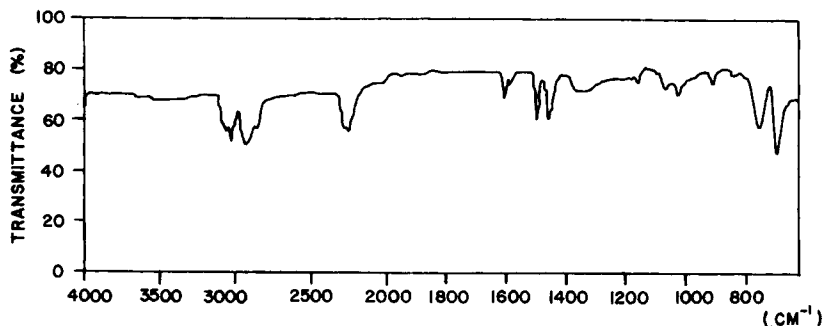


Fig. 1. The ir spectrum of the terpolymer styrene-acrylonitrile-styrylisocyanate (Exp. No. 74/7).

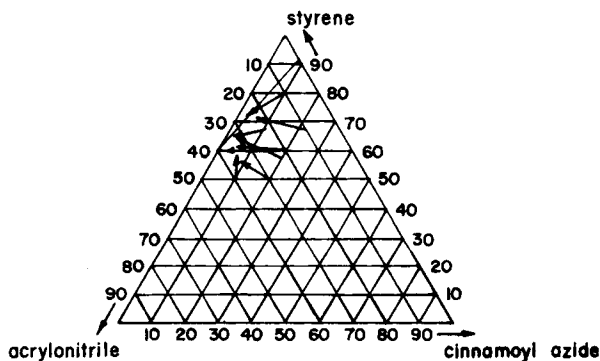


Fig. 2. Monomer-terpolymer triangular composition plots for the styrene-acrylonitrile-cinnamoyl azide system.

All terpolymers investigated are soluble in methyl ethyl ketone and in dimethylformamide but are insoluble in petrol ether (bp: 40–60°C). Terpolymers, containing more than 35 mol % acrylonitrile, are insoluble in benzene.

Quite similar to the behavior of the copolymer styrene–styrylisocyanate, the isocyanate groups in the obtained terpolymers are stable at normal atmospheric conditions. Heating the terpolymers with ethanol or *n*-laurylamine, the typical ir absorption band of the isocyanate group at 2260 cm⁻¹ disappeared. Instead, after reaction with ethanol, the carbamate band at 1740 cm⁻¹ appeared, whereas in the reaction product with the amine, the new band of a substituted urea at 1660 cm⁻¹ was obtained. A film of the terpolymer, prepared by evaporation of its solution in dimethylformamide, showed a reduced ir absorption of the isocyanate group at 2260 cm⁻¹ and three new absorptions at 1670, 1390, and 1100 cm⁻¹. This change in the ir spectra has been observed previously for the copolymer acrylonitrile–styrylisocyanate² and has been ascribed to the formation of amidine groups.

The contents of styrene and acrylonitrile in the obtained terpolymers are of the same magnitude as in commercial copolymers of these two monomers. The small percentage of styrylisocyanate in the terpolymers should produce only small changes of their properties in comparison to the styrene–acrylonitrile copolymer; yet the presence of the rather stable isocyanate groups could be useful for crosslinking, grafting, etc. The mechanical and behavior properties of these terpolymers will now be investigated.

References

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